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<b>⑭ Title of the Invention</b>	<b>Ceramic Spray Deposit Formation Method</b>	
	<b>⑯ Patent Application SHO 60-47400</b>	
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**Specification**

1. Title of the Invention  
Ceramic Spray Coating Formation Method

## 2. Scope of Claims

1) It is a ceramic spray coating formation method which is characterized by the spraying of nickel - aluminum alloy, containing aluminum 4 - 22 % by weight; nickel - chrome alloy, containing chrome 15 - 25 % by weight; or nickel - chrome-aluminum, containing chrome 15 - 25 % by weight; or aluminum 4 - 22 % by weight, as the bonding layer on the alloy backing material of aluminum or aluminum alloy that is heated to a temperature of 250° or up to 400°C, wherein subsequently ceramic material is sprayed on the said bonding layer.

2) It is the method in paragraph 1 of the Scope of Claims paragraph which is characterized by the fact that the ceramic material is a fully stabilized zirconia series material.

## 3. Detailed Description of the Invention

## (Subject Matter of the Invention)

The present invention is concerned with the method of forming a spray coating.

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**(Conventional Technology)**

A member of framework for internal combustion engines is required in order to endure continuous operation for long periods in a high temperature state; and moreover, mechanical strength, as well as resistance to heat and corrosion are required because it experiences a thermocycle, and in piston materials there is a high demand for spray coating with peeling resistance, particularly when using a thermal spray material for items such as the piston head of an internal combustion engine.

For example, although at first there is a spray coating of Ni - Cr alloy on a Ni base alloy backing material, followed by spraying of ZrO<sub>2</sub> series in a gas turbine, the disadvantage is that peeling of the spray coating commonly occurs while the turbine is being used.

In addition, the results of the practical use test of the piston material made of cast steel, which is conducted by spray coating with Ni - Cr alloy followed by spray coating with ZrO<sub>2</sub> whereby, as expected, peeling of the sprayed layer occurs, consequently demonstrate that the thickness of ZrO<sub>2</sub> should be made sufficiently thin to prevent peeling; however, this would require a sacrifice in thermal resistance and resistance to wear.

Furthermore, as a result of having tried the method in which thermal spraying is conducted with ZrO<sub>2</sub> for thermal insulation following the bond-coating of Ni - Cr alloy or Ni - Al material on the surface of the piston made of Al alloy, it is known that this thermal spraying method will not be able to bear up to use because of peeling of the sprayed layer within a comparatively short time, as shown by a practical use engine test.

The reason that such peeling occurs is that there is a difference in the coefficient of thermal expansion between the backing material and the oxide layer of the thermal spray finish layer. That is to say, if the coefficients of thermal expansion for each of the above materials are measured, the results such as those obtained in table 1 and the differences in the coefficients for thermal expansion of each material would be remarkable.

(Table 1)

Materials	Coefficient of Linear Expansion ( $\times 10 - 6/\text{°C}$ )
Al Alloy of Al Alloy Piston	18~24
Cast Steel Backing Material	11~12
Ni Base Backing Material	10~13
Ni - Cr Spray Coating	16.0
Ni - Al Spray Coating	15.0
ZrO <sub>2</sub> Series Spray Deposit	9~11

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The Al or Al alloy in the present invention includes pure Al, Al - Mg series, Al - Si series, Al - Mg - Si series, Al - Si - Ca series, and Al - Si - Fe series.

In addition, Ni - Cr alloy, Ni - Al alloy or Ni - Cr - Al alloy, which are used as base materials, are powders of comparatively coarse-grain in the range of 105~20  $\mu\text{m}$  respectively and the use of such powders is desirable for improving the bonding strength of these materials with the ceramic spray coating. It is necessary to have: a quality of Cr that is 15~25% by weight in the Ni - Cr alloy; a quality of Al that is 4~22% by weight in the Ni - Al alloy; a quality of Al that is 4~22% by weight, and a quality of chrome that is 15~22% by weight in the Ni - Cr - Al alloy. However, according to experimental results, it has been verified that using Al - 20% Si alloy, etc. as a base material has the great effect of improving the bonding strength of the spray coating.

In addition, Ni - Al alloy, and Ni - Cr - Al alloy refer to any of the composite powders, which are coated with Ni or Ni - Cr alloy, ultra-fine granular powders of Ni, Cr, and Al, or metallic bond alloy powders of each component.

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As the table makes evident, in thermal spraying of Ni - Cr alloy on the Al alloy backing material followed by thermal spraying with ZrO<sub>2</sub> in each interval layer, there is a coefficient of thermal expansion difference of approximately  $(2.8) \times 10^{-6}$ /degrees Celsius which leads to peeling of the coating. When examining this kind of peeling part, peeling is often recognized on the border of the surface between the backing material and the bonding layer.

## (Object of the Invention)

The purpose of the present invention is to provide a ceramic spray coating formation method, which shows superior peeling resistance by improvement of the defects in said conventional technology.

## (Constitution of the Invention)

In this invention, it is the ceramic spray coating formation method, which is characterized by the fact that initially Ni - Cr alloy, which contains Cr 15 - 25% by weight, Ni - Al alloy, which contains Al 4 - 22% by weight, or Ni - Cr - Al alloy comprising Ni - Cr alloy, wherein Al 4 - 22% by weight is added and thermally sprayed to form the bonding layer, and subsequently, a stabilized ZrO<sub>2</sub> series ceramic material is thermally sprayed on the surface of this bonding layer.

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One of the characteristic points of the present invention is that the thermal spraying of Al or Al alloy backing material is conducted on the said base material under the heating conditions of 250~400°C as described above. As a result of the many experiments done by our inventors, it was ascertained that the heating effect at temperatures of lower than 250 °C is comparatively weak, and that temperatures higher than 400°C are not only undesirable for this invention because of softening deformation of the backing material but also because the improvement in the bonding strength of the spray coating reaches saturation at temperatures over 400°C. Moreover, it is desirable to conduct bonding immediately after heating up the backing material to a predetermined temperature in a short period of time in order to avoiding deterioration of the backing material, especially when heating it at high temperatures over 350°C. A range of 0.05~0.2mm is suitable for the thickness of the bonding coat because the effect of thermal stress relaxation is weak when the thickness is under 0.05mm; on the other hand, once the thickness exceeds 0.2mm the processing cost of the thermal spraying only increases in cost, while an improvement in effects cannot be expected.

Furthermore, in the present invention, it is desirable that the material for the ceramic thermal spray show excellent high temperature stability, and moreover, low heat conductivity, and furthermore, to have a thermal expansion coefficient that is as close as possible to that of the materials in both the metal for the backing material and the metal for the bonding material.

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There are ceramic materials, such as alumina, mullite, fully stabilized zirconia, calcia, yttria, and magnesia which have these properties, of which fully stabilized zirconia is particularly suitable.

A range of 0.2-10mm is the most suitable thickness for thermal spraying of ceramic material. A thin coating, which is equal to or less than 0.2mm, has the disadvantage of poor thermal insulation; whereas, with a thick coating equal to or more than 1.0mm a decrease in peeling resistance cannot be avoided.

According to the method in the present invention, substances processed by thermal spraying, which are obtained by thermal spraying of oxide ceramic material following thermal spraying of the bonding material on the heated backing material become such that peeling or cracking of the spray coating does not occur even if the substances are used for a long period of time in a thermocycle environment. Therefore, the reason for this is thought to be that the difference in the thermal expansion coefficient among the backing material, bonding material, and zirconia layer has become substantially closer, which is because of the adhesion between the heated backing material and bonding coat layer, which has become remarkably improved as a result of bonding layer adherence, as if the bonding layer had bitten into the backing material, causing expansion in comparison to the backing material that is not heated, and also because zirconia, which has a low thermal expansion coefficient, is thermosprayed on the bonding layer.

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**Bonding layer spray conditions:** The quantity of Ar gas used as arc gas: 38l/min, the used quantity of He gas as auxiliary gas: 7l/min, spraying distance: 110mm, spray coating thickness: 0.1mm/min (Plasmadyne Corporation SG - 100 plasma thermal spraying gun was used)

**Finish layer spray conditions:** Ar gas: 33l / min, He gas: 15l/min, spraying distance: 90mm, spray coating thickness: 0.4mm (Plasmadyne Corporation SG - 100 plasma thermal spray gun was used)

**Thermal cycle test conditions:** The processing which is repeated 10 times involves the test piece being maintained in a furnace at 400°C for 20 minutes, followed by air-cooling.

**Tension test conditions:** The test piece, in which the end face of the spray coated part and the material of another part of pure aluminum were adhered with Araldite AT -1, was used for the tension test.

**Test results:** Each of the tests shows actual measurement values or the mean of five samples.

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(Table 2)

Test Pieces	Backing Materials	Bonding Coat		Finish Thermal Spraying
		Bonding Materials	Backing Material Temperature °C	
1	Pure Al	Ni - 20% Cr	260	Al <sub>2</sub> O <sub>3</sub> • 2% TiO <sub>2</sub>
2	Al - 13% Si	Ni - 18% Cr - 6% Al	340	ZrO <sub>2</sub> • 12% Y <sub>2</sub> O <sub>3</sub>
3	Al - 1.5% Mg	Ni - 5% Al	390	ZrO <sub>2</sub> • 7% CaO
4	Al - 13% Si	Ni - 20% Cr	310	ZrO <sub>2</sub> • 8% Y <sub>2</sub> O <sub>3</sub>

Test Picces	Tension Test		
	Peeling Strength Kg / mm <sup>2</sup>	Average Strength Kg / mm <sup>2</sup>	Peeling Part
1	2.4 - 2.8	2.59	Inside of the Finish Layer
2	2.5 - 2.9	2.76	Same as above
3	2.4 - 3.1	2.74	Same as above
4	2.7 - 3.2	2.92	Same as above

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## (Comparative Example)

Table 3 shows the thermal spraying and the test results according to the same method used in Embodiment 1, in which the same backing material and various kinds of bonding materials, were used and various kind of oxides without heating the backing material or heating at a temperature less than 250°C, or at a temperature equal to or more than 400°C.

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(Table 3)

Test Pieces	Backing Materials	Bonding Coat		Finish Thermal Spraying
		Bonding Materials	Backing Material Temperature °C	
1	Pure Al	Ni - 5% Al	Normal Temperature	Al <sub>2</sub> O <sub>3</sub> · 2% TiO <sub>2</sub>
2	Al - 13% Si	Ni - 20% Cr	120	ZrO <sub>2</sub> · 8% Y <sub>2</sub> O <sub>3</sub>
3	Al - 13% Si	Ni - 20% Cr	210	ZrO <sub>2</sub> · 24% CaO
4	Al - 1.5% Mg	Ni - 20% Al	420	ZrO <sub>2</sub> · 7% Y <sub>2</sub> O <sub>3</sub>

Test Pieces	Tension Test		Peeling Part
	Peeling Strength Kg / mm <sup>2</sup>	Average Strength Kg / mm <sup>2</sup>	
1	2.4 - 2.8	2.59	Between Base Metal - Bonding, Inside of the Finish Layer Same as above
2	2.5 - 2.9	2.76	
3	2.4 - 3.1	2.74	Between Base Metal - Bonding, Inside of the Finish Layer
4	2.7 - 3.2	2.92	

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As described above, according to Embodiment 1 and the comparative samples, the samples that were not heated, or in which a bonding coat was sprayed on the backing material in which the range of heating temperature of the present invention deviated, showed not only low tensile strength but also wide dispersion; however, samples that were processed based on the present invention showed high tensile strength, small dispersion of tensile property, no peeling between the base material and bonding layer, and were broken equally within the finishing layer, and consequently the improvement of the peeling resistance was clearly suggested.

## (Embodiment 2)

After conducting the same thermospraying as Embodiment 1, No. 4, and comparative sample example No. 2 on the top of Lo-Ex Al alloy piston of 50mm  $\phi$  in diameter, during intermittent operation of 10 hours operation and 1 hour shut down, using an actual gasoline engine with conditions of 125 cc, 5000 cycle/min, and as a result, the former did not show any abnormality, such as peeling or cracking on the spray coating following the 20 cycle operation test. However, the latter showed approximately 30% missing on the piston top spray coating by examination of the inside of the engine after the second cycle.

From the above-mentioned results, it is obvious that the peeling resistance of the spray coating formed by the above-mentioned results based on the method of the present invention is extremely good.

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## TRANSLATOR CERTIFICATION

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I, Hirohisa Oda, a translator fluent in the Japanese language, on behalf of Morningside Evaluations and Consulting, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

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⑮ 発明の名称 セラミック溶射皮膜形成方法

⑯ 特願 昭60-47400

⑰ 出願 昭60(1985)3月12日

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明細書

1. 発明の名称

セラミック溶射皮膜形成方法

2. 特許請求の範囲

1) 溫度 250°Cないし 400°Cに加熱したアルミニウムまたはアルミニウム合金基材に、下地層としてアルミニウム 4~22重量%を含有するニッケルーアルミニウム合金、またはクロム15~25重量%を含有するニッケルークロム合金、あるいはクロム15~25重量%とアルミニウム 4~22重量%を含有するニッケルークロムーアルミニウム合金のうちいずれか1種を溶射し、次いで該下地層の上にセラミック材料を溶射することを特徴とするセラミック溶射皮膜形成方法。

2) セラミック材料が安定化ジルコニア系材料であることを特徴とする特許請求の範囲第1項の方法。

3. 発明の詳細な説明

(発明の対象)

本発明は溶射皮膜を形成する方法に関するもの

である。

(従来技術)

内燃機関用部材は長期にわたり高温状態で連続運転に耐え、しかも熱サイクルを受けるため耐熱耐食性と共に機械的強度を要求され、とくに内燃機関のピストンおよびピストンヘッド材等はそれが溶射材である場合には溶射皮膜の耐剥離性に対して高度な要求がある。

たとえばガスタービンにおいてはNi基合金基材上にまづNi-Cr合金を溶射し更にその上に ZrO<sub>2</sub>系セラミックを溶射したものがあるが断続な皮膜はタービン使用中に溶射皮膜の剥離を生じやすい欠点がある。

また、鉄鋼製ピストン材の表面にNi-Cr合金を溶射し更にその上に ZrO<sub>2</sub>を溶射したものを利用試験した結果はやはり溶射皮膜の剥離が生起し易く、したがって剥離を防ぐには ZrO<sub>2</sub>の溶射厚さを薄くしなければ使用出来ないがこれによって耐熱性および耐摩耗性を犠牲にしなければならない。

さらに、Al合金製ピストンに対し、その表面にNi-Cr合金またはNi-Al材を下地溶射したのち、ZrO<sub>2</sub>を溶射して断熱する方法を試みた結果は実用エンジン試験によって比較的短時間内に溶射層の剥離を生じ使用に堪えなくなることが知られている。

斯様な剥離原因是基材と溶射仕上げ層の酸化物層との熱膨張係数の差異が大なるためである。すなわち上記各材の熱膨張係数を測定すれば第1表のような結果が得られ、各材質の熱膨張係数の差異は顕著である。

(第1表)

材 質	線膨張係数 ( $\times 10^{-6}/^{\circ}\text{C}$ )
Al合金ピストンの Al合金	1.8 ~ 2.4
鉄鋼基材	1.1 ~ 1.2
Ni基合金基材	1.0 ~ 1.3
Ni-Cr溶射皮膜	1.6 ~ 0
Ni-Al溶射皮膜	1.5 ~ 0
ZrO <sub>2</sub> 系溶射皮膜	9 ~ 1.1

本発明に謂うAlまたはAl合金とは純AlまたはAl-Ni系、Al-Si系、Al-Ni-Si系、Al-Si-Ca系、Al-Si-Fe系を含むものである。

また下地材として使用されるNi-Cr合金、Ni-Al合金またはNi-Cr-Al合金はそれぞれの粒度105~20μmの範囲の比較的粗粒の粉末であり、斯様な粉末の使用によりセラミック溶射皮膜との接合強度向上のために好ましい。Ni-Cr合金においてはCr品位が15~25重量%、Ni-Al合金においてはAl品位が4~22重量%、Ni-Cr-Al合金においてはAl品位が4~22重量%、クロム品位が15~25重量%であることを要する。しかし実験結果によればAl-20%Si合金等も下地材として溶射皮膜の接合力向上効果は大であることが確認されている。

なおここにいうNi-Al合金、Ni-Cr-Al合金とは、Ni又はNi-Cr合金に被覆された複合粉末あるいはNi,Cr, Alの微粉造粒粉末、又は各成分の金属結合合金粉末のいずれであっても良い。

復から明らかに通りAl合金基材上にNi-Cr合金を溶射し更にZrO<sub>2</sub>溶射したものは各層間ににおいて、ほぼ $(2 \sim 8) \times 10^{-6}/^{\circ}\text{C}$ の熱膨張率差があり、皮膜剥離の原因をなすことは明白である。斯様な剥離部分をしらべると、しばしば基材と下地層との境域面において剥離を認めることができるのである。

## (発明の目的)

本発明の目的は上記従来技術の欠点を改良し耐剥離性にすぐれたセラミック溶射皮膜の形成方法を提供することにある。

## (発明の構成)

本発明は250~400°Cに加熱したAlまたはAl合金基材にまずCr15~25重量%を含むNi-Cr合金またはAl4~22重量%を含むNi-Al合金あるいは前記Ni-Cr合金にAl4~22重量%を添加したNi-Cr-Al合金を溶射して下地層を形成し、次いでこの下地層の表面に安定化ZrO<sub>2</sub>系セラミック材を溶射することを特徴とする溶射皮膜形成方法にある。

本発明の特徴の一つは前記した通りAlまたはAl合金基材を温度250~400°Cに加熱した状態において上記下地材を溶射する点にある。本発明者は多數の実験の結果、基材加熱温度:250°C以下においては加熱の効果は比較的弱く、また400°Cを超えるときは基材の軟化変形を生じ易いのみならず溶射皮膜の接着力向上効果も飽和に達するため400°C以上の加熱は本発明達成のため好ましくないことが確認された。なお基材の加熱に際しては、特に850°C以上の高温加熱の場合は、基材の変質をさける為、短時間の加熱で所定温度とし、すみやかに下地溶射することが望ましい。下地溶射の厚さは、0.05~0.2mmの範囲が適しており、0.05mm以下では熱応力緩和の効果が弱く、一方0.2mmを超えると溶射加工費がかさむのみで効果の向上は期待できない。

また本発明にいうセラミック溶射材は高温安定性良好で、しかも熱伝導率が低く、更に熱膨張係数は可能な限り基材金属ならびに下地材金属の熱膨張係数に近いものが良い。斯様な性質を有する

セラミック材としてはアルミナ、ムライト、安定化ジルコニア、カルシア、イットリア、マグネシア等があげられるが、特に安定化ジルコニアが好適である。

セラミック材の溶射厚さは0.2~1.0mmの範囲が最適である。0.2mm以下の薄い皮膜は断熱効果に乏しい欠点があり、また1.0mm以上の厚い皮膜は耐剥離性低下はまぬがれない。

本発明の方法により加熱された基材に下地材を溶射後、酸化物セラミック材を溶射することによって得られる溶射加工体は熱サイクル環境下において長期間使用しても溶射皮膜の剥離、亀裂等を生起しないものとなる。その理由は加熱基材と下地溶射層の密着性は基材を加熱しない場合に比較して膨張状態の基材に下地層が吸い込むごとく溶射されるため密着性をいちじるしく向上するのに加え、この下地層に熱膨張係数の低いジルコニアが溶射されるため結局、基材、下地材およびジルコニア層の熱膨張係数の差異を実質的に接近せしめる効果が発揮されるためと考えられる。

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下地層溶射条件：アーケガスとしてArガス使用量38L/min、補助ガスとしてHeガス使用量7L/min、溶射距離110mm、溶射皮膜厚さ0.1mm（プラズマダイン社SG-100 プラズマ溶射ガン使用）

仕上げ層溶射条件：Arガス38L/min、Heガス15L/min、溶射距離90mm、溶射皮膜厚さ0.4mm（プラズマダイン社SG-100 プラズマ溶射ガン使用）

熱サイクル試験条件：溶射後の試片を400°Cの炉内に20分間保持後空冷する過程を10回繰り返す。

引張り試験条件：熱サイクル試験後の試片の端面溶射皮膜部と相手材純アルミニウムを接着剤アラルダイトAT-1にて接着後引張り試験に供す。

試験結果：各試験とも5試料の実測値または平均値。

(以下余白)

本発明において安定化ジルコニアを使用する理由は次の通りである。

安定化ジルコニアとは、加熱・冷却において特定温度で変態しその際急激な体積変化を起す純ジルコニアに対し $Y_2O_3$ 、CaO、MgO等が数%以上添加され、常温から高温まで変態による急激な体積変化を起きない構造をしたジルコニアである。又ジルコニアの熱膨張係数が金属に近く高いことから熱サイクルを受ける部材のコーティングに対しクラック等が生じにくく最適である。

## (実施例1)

純Al、Al-13%Si合金およびAl-1.5%Mg合金基材にNi-Cr合金、Ni-Al合金またはNi-Cr-Al合金を250~400°Cに加熱された基材上に溶射し、次いで各種酸化物粉末を仕上げ溶射した試片について熱サイクル処理後、溶射皮膜の引張り試験を行い皮膜の耐剥離性をしらべた。溶射条件、熱サイクル試験条件および引張り試験条件は次に示す通りであり、試験結果を第2表に示す。

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(第2表)

試片	基材	下地溶射		仕上げ溶射
		下地材	基材温度 °C	
1	純Al	NI-20%Cr	260	Al <sub>2</sub> O <sub>3</sub> ・2%TiO <sub>2</sub>
2	Al-13%Si	NI-18%Cr-6%Al	340	ZrO <sub>2</sub> ・12%Y <sub>2</sub> O <sub>3</sub>
3	Al-1.5%Mg	NI-5%Al	390	ZrO <sub>2</sub> ・7%CaO
4	Al-13%Si	NI-20%Cr	310	ZrO <sub>2</sub> ・8%Y <sub>2</sub> O <sub>3</sub>

試片	引張り試験		
	剝離強度 Kg/mm <sup>2</sup>	平均強度 Kg/mm <sup>2</sup>	剝離部位
1	2.4~2.8	2.59	仕上げ層内
2	2.5~2.9	2.76	同上
3	2.4~3.1	2.74	同上
4	2.7~3.2	2.92	同上

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## (比較例)

実施例1と同一基材と各種下地材および各種酸化物を用い、基材を加熱せず、または250°C以下もしくは400°C以上の加熱状態において実施例1と同様の方法により溶射および試験を行なった結果、第3表に示す結果を得た。

(以下余白)

(第3表)

試片	基材	下地溶射		仕上げ溶射
		下地材	基材温度 °C	
1	純Al	NI-5%Al	常温	Al <sub>2</sub> O <sub>3</sub>
2	Al-13%Si	NI-20%Cr	120	ZrO <sub>2</sub> ·8%Y <sub>2</sub> O <sub>3</sub>
3	Al-13%Si	NI-20%Cr	210	ZrO <sub>2</sub> ·24%MgO
4	Al-1.5%Mg	NI-20%Al	420	ZrO <sub>2</sub> ·7%CaO

試片	引張り試験		
	剝離強度 Kg/mm <sup>2</sup>	平均強度 Kg/mm <sup>2</sup>	剝離部位
1	1.3~2.1	1.56	母材-下地間、仕上層内
2	1.9~2.3	2.32	同上
3	2.2~2.5	2.31	母材-下地間
4	1.9~2.6	2.15	仕上層内

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以上、実施例1および比較例を見るに、加熱せず、または本発明の加熱温度範囲を逸脱する温度に加熱した基材に下地溶射を施したもののは引張り強度が低いのみならず強度のばらつきが大であるのに対し本発明方法によれば引張り強度は高く、引張り特性にはばらつきが少く、母材-下地間での剥離も見られず、仕上層内で安定して破断していることから判断して本発明方法により耐剝離性の改善は顕著であることが知られる。

## (実施例2)

径50mmのローエックスAl合金製ピストンの頂部に実施例1、No.4および比較例No.2と同様の溶射を行なった後 125cc、5000サイクル/分のガソリンエンジン実機において10時間運転 1時間停止の間けつ運転でエンジンテストを実施した結果、前者は20サイクルの運転テスト後においても溶射皮膜に剥離、亀裂等の異常は全く観察されなかった。しかしに後者は2サイクル目の運転後エンジン内を調べたところ、ピストン頂部溶射皮膜の約30%に欠落が観察された。

以上の結果から本発明方法によって形成された溶射皮膜の耐剝離性は極めて良好であることは明らかである。

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